

MOLECULAR AND CRYSTAL ORBITAL STUDIES OF ORGANIC CRYSTAL FORMATION

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Abstract

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Ab initio molecular orbital and crystal orbital methods are applied to the study of the geometry of hydrogen-bonded organic crystals and to predict the relative stability of polymorphic modifications. Cluster calculations of para-benzoquinone, of urea and of thiourea at HF, DFT, and AM1 levels with pseudotranslational constraints allow for the analysis of the energies for each type of H-bonds and their dependence on the cluster size. Periodical calculations on infinite systems are in good agreement with the results of cluster calculations. The cooperative components of intermolecular interaction, which are neglected in the most empirical force-field models account for up to 30% of the total interactions in the systems considered. This non-additivity is shown to lead to experimentally observed differences in crystal packing between urea and thiourea, and can be successfully reproduced at the practically justified approximations.

One important application of MO calculations is to build simple yet accurate models for intermolecular interactions. Modifications of the basis set by optimizing the centroid positions of each basis function (floating basis set) combined with

semiempirical values for exponent factors are suggested for this purpose. Such a wavefunction satisfies the Hellman-Feynman theorem and its electron density can be exactly represented by point charges.

The methodology developed in this work, may be applied to the rational design of crystals with required properties. This will be useful to solve practical problems of crystal engineering, and material science.

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CHAPTER 1

1. INTRODUCTION

The purpose of this thesis is to apply *ab initio* molecular orbital (MO) and crystal orbital (CO) methods to interpret geometry of organic crystals. The methods are also applied to prediction of relative stability of polymorphic modifications. Success in the interpretation and prediction of organic crystal structures will assist material science in synthesizing the materials with particular properties. It will also advance the understanding of the structure for other condensed phases such as liquids and biopolymers. The results are discussed in the framework of the contemporary state of the field. In this study the supermolecular (cluster) and periodical approaches were applied to crystals with H-bonds at different levels of theory: semiempirical, Hartree-Fock (HF), and post-HF. It will be shown that the cooperative component of intermolecular interaction can be as large as 30% of the total interaction. On the example of urea and thiourea we will show how this cooperativity can lead to experimentally observable differences in crystal packing, and can be successfully reproduced with practically justified approximations.

Chapter 2 gives a brief overview of the methods for solid-state simulations. The existing methods of organic crystal structure predictions require a large number of energy evaluations, making the application of the empirical force field method a necessity. In many cases additive approximations are used for simplification. Some of them employ *ab initio* calculations to fit the force field parameters. The empirical

force-field approach has proved effective, but its applicability to the novel system types is uncertain. *Ab initio* methods of crystal calculation (both periodical and cluster approach) are far more reliable. At present no code for calculation of analytical derivatives for the periodic system is publically available, which makes geometry optimization unfeasible. The cluster approach makes the use of existing program packages for molecular *ab initio* calculations, and allows to analyze components of molecular interactions in details. However, this approach yields results for finite aggregates and it is applicable to periodical systems in asymptotic limits only.

Chapter 2 also summarizes the data on the molecular, cluster, and crystal structures of urea and thiourea. It addresses the consistency of *ab initio* calculations and experiments on energies and geometries of these systems. The joint application of single-point cluster and periodical calculations based on known crystal structure is applied in Chapter 3 to the case of crystalline benzoquinone, urea, and thiourea. When the crystal structure is not experimentally known, single point calculations are no longer applicable. This necessitates a thorough investigation based on constrained geometrical optimization of molecular clusters of different sizes. The results of such an investigation applied to urea and thiourea are reported in Chapters 4, 5 and 7 (for dimers, one- and two/three-dimensional clusters respectively).

One of the important applications of MO calculations at the high level of theory is to build simple yet accurate models for intermolecular interactions. Our attempts to build such a model in order to simulate *ab initio* data, as well as our suggestions for its improvements, are described in Chapter 6. According to the Hellman-Feynman theorem, forces on nuclei in the molecular system can be calculated classically from the charge density of the molecule. Therefore, when building an

electrostatic model, one has to make sure that (a) wavefunction complies with the Hellman-Feynman theorem, and that (b) electron density is reproduced by classical charge distribution to an acceptable approximation. By comparing classical charge distribution schemes in the form of different partial atomic charge separation methods, we found that the *ab initio* values on interaction energy in the urea chain dimer are best reproduced by Mulliken charges. These charges are used to describe polarization effects in larger chain clusters. Chapter 6 also describes the modifications to the basis set by optimizing centroid positions of each basis function. This, in turn, allows the wavefunction to satisfy Hellman-Feynman theorem. The resulting charge distribution is also significantly improved so that the residual electric field in the nuclei of the optimized molecule vanishes. Since the existing codes are not well suited to handle the floating basis sets, these calculations present a computational challenge. However, floating basis set allows to decrease the number of the basis functions N to the minimum, thus greatly reducing computational costs while maintaining built-in polarization flexibility of the basis set. We suggest a semiempirical approach to optimizing parameters of this minimal floating basis set. The ability of the wavefunction in the form of a minimal floating basis set to be exactly represented by point charges opens the possibility of building classical and combined models based on the described wavefunction. Finally, we discuss some donor-acceptor models, alternative to the electrostatic description of H-bonds.

The methodology developed in this work could be applied to the rational design of crystals with desirable properties to solve practical problems of crystal engineering and material science.